

Influence of particle oxide coating on light scattering by submicron metal particles on silicon wafers

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Abstract

We report the effect of room-temperature oxidation on scattering of 633 nm light by copper particles deposited on a silicon wafer. The results provide a validation for a theory of light scattering by coated particles on a substrate and establish the lifetime of these particles as light scattering standards to be on the order of a few months. The results also suggest that the room-temperature oxidation of copper particles proceeds in a continuous manner, rather than approaching an asymptotic thickness as found by Cabrera and Mott [Rep. Prog. Phys. **12**, 163 (1948)] on copper films.

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Recently, we reported the development of metal nanoparticles for calibrating light scattering instrumentation, such as that used to detect particles on silicon wafers.¹ Dielectric particles are commonly used because nearly monodisperse polystyrene (PS) spheres are commercially available. Metallic particle standards are of interest in scattering metrology because the scattering by metallic particles can differ substantially from that by dielectric particles of the same size. In particular, metallic particles provide a rigorous test for the accuracy of theories for light scattering by particles attached to surfaces, since the interaction of metallic particles with a substrate can be much stronger than that of dielectric particles and can have a significant effect on the scattering behavior. Furthermore, metallic particles may be more representative of particles found in production environments. In this letter, we describe the time-evolution of the oxidation and the resulting scattering behavior of copper spheres on a silicon wafer exposed to typical laboratory atmospheric conditions.

Hydrogen-free spray pyrolysis, followed by electrostatic classification, was used to generate copper spheres having diameters of 100 nm and 140 nm with size distributions having standard deviation of 3 nm.^{2,3} Using an electrostatic precipitator, these spheres were deposited onto a silicon wafer (140 nm spheres) for light scattering experiments and a transmission electron microscopy (TEM) grid (100 nm spheres) for imaging, with a particle number density of approximately 500 mm⁻². The wafer and TEM grid were then stored in plastic containers exposed to atmospheric pressure at room temperature (22 °C ± 2 °C), and periodically removed to perform light scattering measurements and TEM. The relative humidity ranged from 15 % (winter) to 40 % (summer) during the year.

A thin coating (a few Å in thickness) on the copper spheres could be observed in TEM the day after production, a result observed on copper films by other researchers.⁴ Figure 1 shows three representative images taken after 3 weeks, 18 weeks, and one year. Figure 2 shows the oxide thickness y determined from TEM images as a function of time t . The oxidation proceeds in an approximately linear fashion. The growth

function, obtained by a weighted linear least-squares fit, is $y \text{ (nm)} = 0.031 \times t \text{ (days)}$ with an r^2 -correlation coefficient of 0.992. The 95 % confidence uncertainty in the rate is 0.004 nm/d.

The resulting copper oxide phases can be either cuprous oxide (Cu_2O) or cupric oxide (CuO) depending on temperature and oxygen concentration. At room temperature, however, Cu_2O is the dominant product of oxidation,⁵ and the Cu_2O film can be terminated by a few monolayers of cupric oxide (CuO) products at the air interface.⁴ To properly use these particles in scattering measurements, we need to determine the oxide composition because Cu_2O and CuO exhibit different optical properties. X-ray diffraction (XRD) measurements ($\text{Cu K}\alpha$) were performed on a polydisperse sample, collected using filtration, after 12 months of storage in a plastic container at room temperature. Figure 3 shows the XRD results for the copper powder immediately after production and after 12 months. Clear evidence of the formation of the crystalline Cu_2O phase is seen in Figure 3(b) at $2\theta = 36.5^\circ$ and $2\theta = 61.4^\circ$, while no crystalline CuO phase ($2\theta = 35.5^\circ$, 38.8° , and 48.7°) is observed.

Figure 4 shows polarized light scattering results for the 140 nm diameter copper spheres on a silicon substrate at the time of production and after 12 months. Light scattering parameters (differential cross section, $d\sigma/d\Omega$, degree of polarization P , normalized degree of circular polarization P_c/P , and the principle angle of polarization η) were measured in the plane of incidence with an incident angle $\theta = 60^\circ$, 45° incident polarization, and wavelength $\lambda = 633 \text{ nm}$. Measurements performed within two months from production were essentially indistinguishable from those taken immediately after production. However, by 12 months a clear change in all of the scattering parameters can be observed.

The theory of Bobbert and Vlieger⁶ has been shown to predict the scattering behavior for spherical particles on surfaces. The theory has been extended to account for the presence of a substrate coating and a particle coating. Included in Fig. 4 are predictions for the scattering parameters for a 140 nm copper sphere above a silicon substrate having a 1.6 nm native oxide coating.⁷ The agreement between the theoretical prediction and the data measured soon after production is very good. A non-linear least-squares fitting routine, letting the particle coating thickness be the only free parameter and fitting to all of the light scattering parameters,⁸ found a particle coating thickness of 15 nm from the data measured 12 months after production. This thickness is within the uncertainty of the thickness observed in Fig. 2. The resulting fit to the theory is included in Fig. 4 and shows reasonable agreement with the experiment. The theoretical prediction for a 7 nm particle coating thickness is also shown, and does not agree well with either of the experimental measurements. We estimate that the copper sphere particles can only be used as a scattering standard for a period of about two months.

Oxidation of metallic materials is an important process in thin film growth, catalysis, and gate oxide formation, while it sometimes causes serious problems in wiring circuit boards and preserving integrity of material standards. Many oxidation studies have been reported for high temperature cases,^{5,9-12} but only a few studies have been done to understand metal oxidation behavior at room temperature conditions.^{4,5} One of the theories of the oxidation of metals was reported by Cabrera and Mott,⁵ for both high and room temperature cases. They found that, for example, Cu_2O growth at room temperature is initially very rapid when exposed to oxygen, but growth slows remarkably within an hour after a critical thickness of approximately 10 nm is reached. This behavior is relatively insensitive to oxygen pressure. They found that Cu_2O growth nearly ends within about 5 h at room temperature once a thickness of 13 nm is reached. Their results differ from the results presented here, where we observe an approximate linear growth over a period of a year.

Yang *et al.*⁹ reported Cu_2O film formation on a Cu substrate at a partial pressure between $7 \times 10^{-3} \text{ Pa}$ and 10^5 Pa at temperatures between 60°C and 600°C . They noted only epitaxial oxide island formation from nucleation to coalescence of Cu_2O for all pressures and temperatures examined. For example, Cu_2O nucleation was visible within 5 min at 13 Pa at 350°C , and the oxide islands grow via coalescence, covering the whole substrate within 25 min. Once coalescence happens, oxidation of copper is self-limited by the change from oxidation of the surface as the limiting step to diffusion of oxygen through the oxide layer becoming the limiting step. Therefore, Yang *et al.*⁹ suggested the self-limiting oxidation rate is due to the

coalescence of oxide islands, not to the uniform passivation film formation of oxide in a layer-by-layer fashion as noted by Cabrera and Mott⁵.

In summary, we report on room temperature oxidation of submicrometer copper particles. Excellent agreement between light scattering measurements and TEM is found. The results also suggest that the room temperature oxidation of copper particles proceeds in a continuous manner, rather than approaching an asymptotic thickness as found by Cabrera and Mott. The results validate a theory of light scattering by coated particles on a substrate, and demonstrate the method of light scattering as a means for measuring particle coating thickness. Furthermore, it is found that the lifetime of such particles as light scattering standards is limited by the growth of this oxide layer to a few months.

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References and Footnotes

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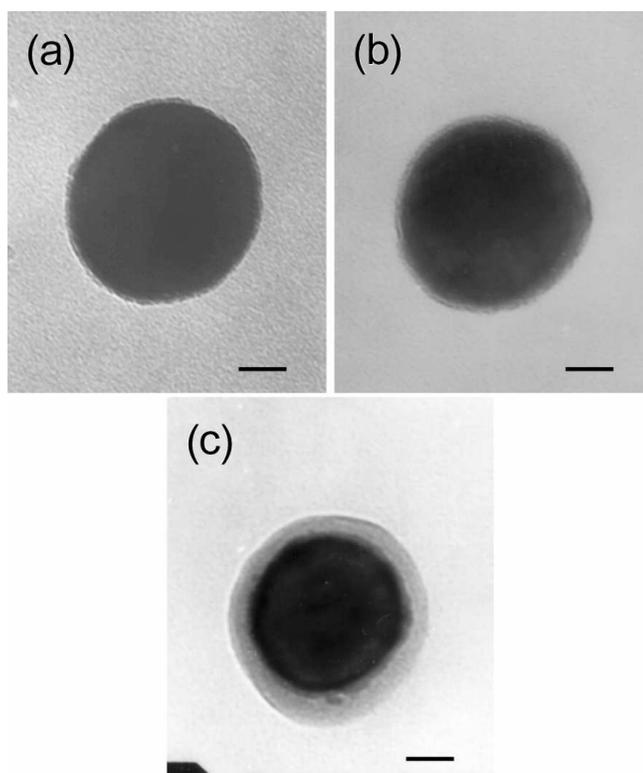


FIG. 1. TEM images of copper spheres showing the growth of oxide coating after three weeks (a), after 18 weeks (b), and after 12 months (c), at room temperature. The length of the bar is 25 nm.

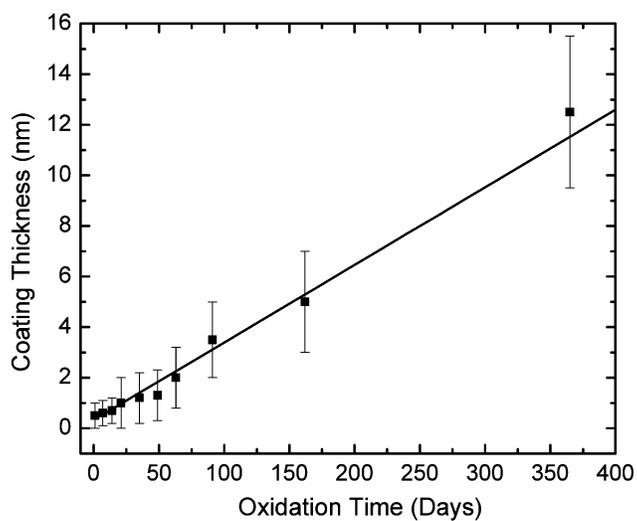


FIG. 2. Growth of the copper oxide thickness on the copper spheres at room temperature. The uncertainties shown represent 95 % confidence levels.

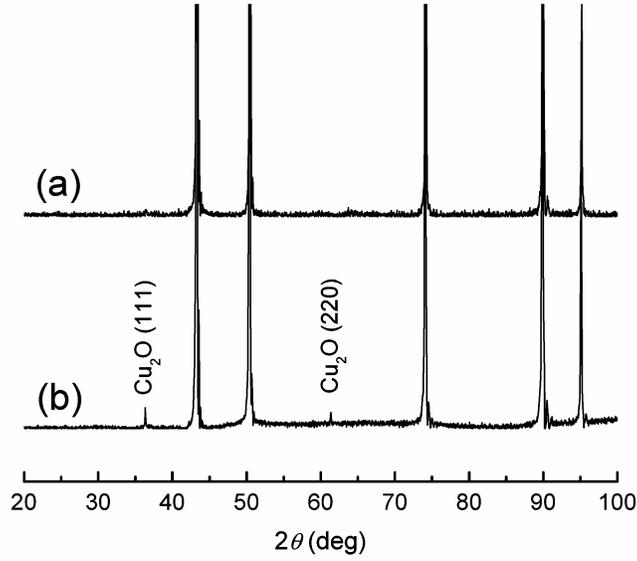


FIG. 3. X-ray diffraction from copper powder. Curve (a) was measured shortly after production and curve (b) was measured after 12 months. Intensities are reported in arbitrary units.

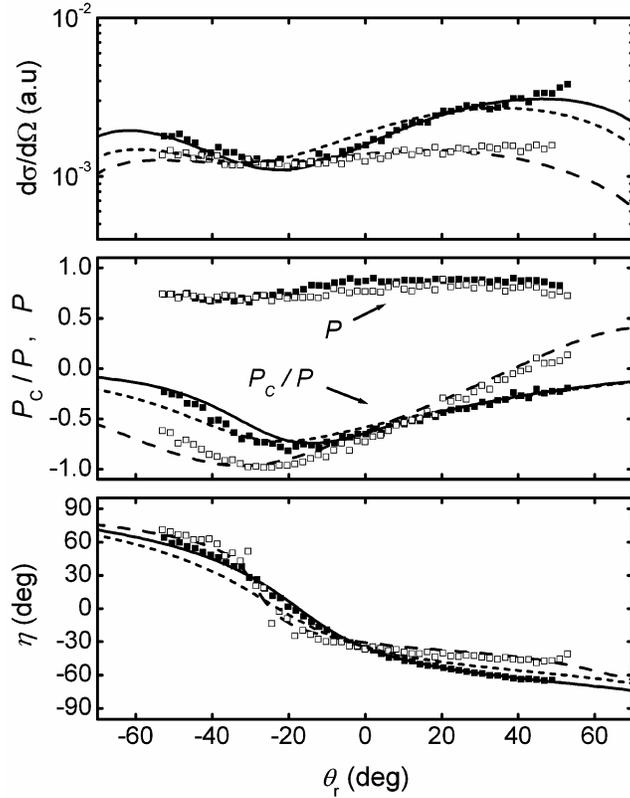


FIG. 4. The differential scattering cross section ($d\sigma/d\Omega$), the degree of polarization (P), the normalized degree of circular polarization (P_c/P), and the principal angle of the polarization (η) measured for 140 nm copper spheres deposited on a silicon wafer using 45 deg polarized incident light. Filled squares were measured for copper spheres at the time of production, and hollow squares were measured for copper spheres after 12 months. The solid, dotted, and dashed curves were calculated for copper spheres with no coating, 7 nm coating, and 15 nm coating, respectively.